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(21) International Application Number: PCT/US89/02669 (22) International Filing Date: 22 June 1989 (22.06.89) (30) Priority data: 210,554 23 June 1988 (23.06.88) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: RAO, V., N., Mallikarjuna ; 1 Georgetown Avenue, Wilmington, DE 19809 (US). (74) Agent: WOLFSON, Herbert, M.; E.I. du Pont de Nemours and Company, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), SU. Published <i>With international search report.</i>
(54) Title: CATALYZED HYDROFLUORINATION OF ALKENES (57) Abstract Process for the preparation of fluorinated alkanes by contacting alkenes with HF in the presence of TaCl ₅ or TaBr ₅ .		

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INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/02669

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : C 07 C 17/00, C 07 C 19/08		
II. FIELDS SEARCHED		
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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4258225 (FEIRING) 24 March 1981 cited in the application <div style="text-align: center;">-----</div>	
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>" " document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
6th September 1989	29. 09. 89	
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EUROPEAN PATENT OFFICE	<div style="text-align: right; font-weight: bold; font-size: 1.2em;">T.K. WILLIS</div>	

Catalyzed Hydrofluorination of Alkenes
CROSS-REFERENCE TO RELATED APPLICATION

5 This application is a continuation-in-part
of U.S. application Serial No. 07/210,554 filed
June 23, 1988

FIELD OF THE INVENTION

10 Process for the preparation of fluorinated
alkanes by contacting alkenes, preferably halogenated
alkenes, with hydrogen fluoride in the presence of
TaCl₅ or TaBr₅.

BACKGROUND OF THE INVENTION

A. E. Feiring, Journal of Fluorine
15 Chemistry, 13, 7-18 (1979) discloses the use of
tantalum pentafluoride as a catalyst for the addition
of hydrogen fluoride to tetra- and trichloroethene and
related compounds. The catalyst is also useful for
fluorine chlorine exchange reactions. However, under
20 the conditions of the batch experiments, catalysts
such as BF₃, TaCl₅, Ta₂O₅, CoF₃, V₂O₅, ZrCl₄, NbCl₅,
HgO, and WCl₆ showed no catalytic activity at 150°C
for the addition of HF to tetrachloroethene.

The use of tantalum pentafluoride as a
25 catalyst for the addition of hydrogen fluoride to
unsaturated compounds has been disclosed and claimed
in U.S. 4,258,225.

SUMMARY OF THE INVENTION

This invention is a process for the
30 preparation of fluorinated alkanes by contacting, at a
temperature of about 0°C to about 185°C under sub-
stantially anhydrous conditions, one molar equivalent
of an alkene, preferably a halogenated alkene,
selected from alkenes of the following formulas

35 $R^1R^2C=CR^3R^4$ and $R^5R^6C=CR^7R^8$

wherein

US 8902669
SA 29736

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

preferably from 0.001 to 0.250 mole, per mole of starting alkene for reasons of economy and effectiveness. The catalyst is a commercially available crystalline solid and can be used alone or
5 on a support, such as carbon.

The preferred halogenated alkenes are where at least two, and more preferably at least three, of R^1 , R^2 , R^3 or R^4 are Cl. Where at least one of R^1 , R^2 , R^3 or R^4 is C_xZ_{2x+1} , it is preferred that x is 1
10 to 3 and, more preferably x is 1. The specifically preferred alkenes are $Cl_2C=CCl_2$, $HClC=CCl_2$, $HFC=CF_2$, $ClFC=CF_2$, $H_2C=CCl_2$, $H_2C=CF_2$, and $H_2C=CHCl$.

The reaction can be carried out in the liquid phase or vapor phase and at autogenous
15 pressures or under constant pressure ranging from atmospheric to superatmospheric. Both the liquid phase and vapor phase processes include batch, semicontinuous and continuous modes of operation.

The reaction can be carried out at from
20 about 0°C to about 185°C. The preferred temperature is about 35°C to about 175°C.

Anhydrous or substantially anhydrous conditions means that water, which is detrimental to the reaction, should be excluded as much as possible
25 from the reaction zone. The HF which is commercially available as anhydrous grade can be used in the reaction directly. Exclusion of moisture from the reaction vessel by means of appropriate moisture traps or other means is a routine procedure and is well
30 known in the art.

It is preferred that 1 to 30 molar equivalents of HF be utilized, and more preferably from 3 to 30 molar equivalents of HF. At least 5 molar equivalents of HF is preferred, particularly for
35 highly chlorinated alkenes such as $Cl_2C=CCl_2$. In practice from 15 to 30 molar equivalents of HF ensures

5 R^1, R^2, R^3, R^4 and R^5, R^6, R^7, R^8 are each selected from the group represented by C_xZ_{2x+1} , wherein Z is H, F, Br, or Cl and wherein $x = 0$ to 10, preferably with the proviso that in at least one of R^1, R^2, R^3 and R^4 and in at least one of R^5, R^6, R^7 and R^8 , Z is F, Br or Cl; and

10 at least one of the pairs R^5 and R^6, R^7 and R^8, R^5 and R^7 , and R^6 and R^8 taken together is $-(CH_2)_n-$ wherein "n" is an integer from 2 to 7, with the proviso that when R^5 and R^7 and/or R^6 and R^8 are trans, "n" must be 6 to 7, and when only two of the group R^5, R^6, R^7, R^8 are combined to form a
15 cyclic structure the remaining two groups may be C_xZ_{2x+1} , wherein Z is H, F, Br, or Cl and $x = 0$ to 10,

with HF in the presence of at least one catalyst selected from tantalum pentachloride and tantalum
20 pentabromide to produce a fluorinated alkane.

DETAILS OF THE INVENTION

The resulting fluorinated alkane produced in accordance with the invention has one hydrogen atom over and above the number of hydrogen atoms originally
25 present in the alkene, and one or more fluorine atoms over and above the number of fluorine atoms originally present in the alkene.

The alkene starting materials of the invention do not substantially react with hydrogen
30 fluoride alone under the conditions of temperature and pressure used in this invention and require the presence of added catalyst, specifically tantalum pentachloride ($TaCl_5$) or tantalum pentabromide ($TaBr_5$).

35 It is preferred that the $TaCl_5$ or $TaBr_5$ be used in an amount from 0.001 to about 5 moles,

In the vapor phase reaction, the reactants are introduced into the reactor above their boiling points. The temperature of the reactor must also be sufficient to keep the products of the reaction in the vapor state so that they pass over into a cooled receiver beyond the reactor rather than remain in the catalyst zone for a prolonged period of time.

For vapor phase reactions, it is convenient to support the TaCl_5 or TaBr_5 on an inert porous material such as carbon or other known supports. The preferred catalyst is TaCl_5 . The amount of catalyst to inert support is from 10% to 50% by weight with amounts of about 25% being preferred. The amount of HF used in the reaction is from 1 to 30 molar equivalents per mole of organic starting material. The reaction can be carried out at from about 50°C to about 185°C . The preferred temperature is about 70°C to about 175°C . The contact time of the reagents with the catalyst may be specified instead of reaction time. The combined operations of feed rate, control of reactor temperature and pressure and rate of removal of product from the reactor influence the residence time of the product in the reactor. It may be desirable to shorten the residence time for a given product within the reactor to control the formation of undesired products. Contact time is the average time that the reactant product mixture is in contact with the catalyst. Broadly, contact times of from 0.1 to 25 seconds are useful with preferred contact times in the range of 1 to 10 seconds.

Under the reaction conditions set forth above, a portion of the TaCl_5 or TaBr_5 may undergo fluorination, so that a portion of the TaCl_5 or TaBr_5 may be in the form of $\text{TaCl}_{5-x}\text{F}_x$ or $\text{TaBr}_{5-x}\text{F}_x$ where "x" may be from 0 to about 5. The instant invention

the best combination of economics and fluorination yield.

The reaction vessel is constructed from materials which are resistant to the action of
5 hydrogen halide such as nickel alloys, including monel, "Hastelloy" and "Inconel".

The liquid phase reactions are conducted by introducing the reagents in any order into the reaction vessel. Generally, the $TaCl_5$ or $TaBr_5$ and
10 starting alkene are placed in the reaction vessel which is then cooled, and the required amount of hydrogen fluoride is condensed in the vessel. The vessel may be cooled in Dry Ice or liquid nitrogen and evacuated prior to the introduction of hydrogen
15 fluoride to facilitate addition of the hydrogen fluoride. The contents of the vessel are raised to the appropriate reaction temperature and agitated by shaking or stirring for a length of time sufficient to cause the reaction to occur.

20 For liquid phase reactions, the amount of $TaCl_5$ or $TaBr_5$ used is from 0.001 to about 5 moles per mole of starting alkene, preferably from 0.001 to 0.250 mole, more preferably from 0.005 to about 1 mole per mole of starting alkene but most preferably from
25 0.01 to 0.5 mole per mole of starting alkene. In general, when one uses the higher molar concentration of the catalyst, he can use a lower molar proportion of the HF reactant. The preferred catalyst is $TaCl_5$. The amount of HF used in the reaction is from 1 to 30
30 molar equivalents per mole of organic starting material. The reaction can be carried out at from about 0°C to about 185°C. The preferred temperature is about 35°C to about 175°C. Reaction time can be from 0.5 to 18 hours; the preferred times are from 1
35 to 8 hours.

of tantalum pentachloride and 15 g of anhydrous HF. The reactor was brought to atmospheric pressure with nitrogen. The back pressure regulator was set at 200 psig. The contents were heated and stirred at
5 119-122°C for about four hours. Analysis indicated 43.4% of $\text{CClF}_2\text{CHCl}_2$, 12.1% $\text{CCl}_2\text{FCHCl}_2$, and 30.1% unreacted starting material as the major products.

EXAMPLE 2

The General Experimental Procedure was
10 followed using 8.3 g of tetrachloroethylene, 2.0 g of tantalum pentachloride and 15 g of anhydrous HF. The reactor was pressurized to 200 psig when cold with nitrogen and the back pressure regulator was set for 400 psig. The contents were heated and stirred at
15 135-138°C for two hours. Product analysis indicated 23% CF_3CHCl_2 and 68.9% $\text{CClF}_2\text{CHCl}_2$ as the major products.

EXAMPLE 3

The General Experimental Procedure was
20 followed using 16.5 g of tetrachloroethylene, 4.0 g of tantalum pentachloride and 15 g of anhydrous HF. The reactor was pressurized to 200 psig with nitrogen and the back pressure regulator was set for 500 psig. The contents were heated and stirred at 142-144°C for
25 about one hour. Analysis indicated 69.5% CF_3CHCl_2 , and 27.4% $\text{CClF}_2\text{CHCl}_2$ as the major products.

EXAMPLE 4

Example 3 was repeated with the exception that the reaction was run for 90 minutes. Analysis
30 indicated 88.2% CF_3CHCl_2 and 9.5% $\text{CClF}_2\text{CHCl}_2$ as the major products.

EXAMPLE 5

The General Experimental Procedure was followed using 22.4 g of trichloroethylene, 1.0 g of
35 tantalum pentachloride and 10 g of anhydrous HF. The reactor was pressurized to 200 psig with nitrogen when

is understood to include that condition when it may exist.

Pressure is not critical. Atmospheric, superatmospheric and autogeneous pressures are the most convenient and are therefore preferred.

The fluorinated alkanes produced by the invention have utility as refrigerants, solvents and blowing agents.

EXAMPLES

10 General Experimental Procedure

The reactor consisted of a 100 ml high pressure cylinder made of monel or "Inconel" containing a magnetic stirrer and an internal thermocouple. Mounted on top of the reactor was a condenser and a back pressure regulator connected to an optional on line analytical system. Suitable inlet and exit lines were also present to allow for admission of reactants and withdrawal of products.

To the reactor was charged TaCl_5 in the desired amount. The reactor was then cooled and evacuated. The alkene starting material and the required amount of HF were then admitted to the reactor. The reactor was then pressurized with nitrogen to the desired pressure while still cold and then gradually brought to the desired operating temperature with stirring by using external heat provided with an oil bath. The back pressure regulator was set to the desired operating pressure prior to heating the reactor.

At the completion of the reaction, the product was isolated by conventional means and analyzed by gas chromatography. All the percentages reported in the Examples are area %.

EXAMPLE 1

The General Experimental Procedure was followed using 16.5 g of tetrachloroethylene, 0.45 g

What is claimed:

1. A process for the preparation of fluorinated alkanes by contacting, at a temperature of about 0°C to about 185°C, under substantially anhydrous conditions, one molar equivalent of an alkene selected from alkenes of the following formulas



wherein

- 10 R^1, R^2, R^3, R^4 and R^5, R^6, R^7, R^8 are each selected from the group represented by C_xZ_{2x+1} , wherein Z is H, F, Br or Cl and wherein x = 0 to 10; and

- 15 at least one of the pairs R^5 and R^6, R^7 and R^8, R^5 and R^7 , and R^6 and R^8 taken together is $-(CH_2)_n-$ wherein "n" is an integer from 2 to 7 with the proviso that when R^5 and R^7 and/or R^6 and R^8 are trans, "n" must be 6 to 7, and when only two of the group R^5, R^6, R^7, R^8 are combined to form a
- 20 cyclic structure the remaining two groups may be C_xZ_{2x+1} , wherein Z is H, F, Br or Cl and x = 0 to 10,

- with HF in the presence of at least one catalyst selected from tantalum pentachloride and tantalum pentabromide to produce a fluorinated alkane.
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2. A process for the preparation of fluorinated alkanes by contacting, at a temperature of about 0°C to about 185°C, under substantially anhydrous conditions, one molar equivalent of a halogenated alkene selected from alkenes of the following formulas
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wherein

- 35 R^1, R^2, R^3, R^4 and R^5, R^6, R^7, R^8 are each selected from the group represented by C_xZ_{2x+1} , wherein Z is H, F, Br, or Cl and

cold and the back pressure regulator was also set for 200 psig. The contents were gradually heated to 85-90°C with stirring and maintained at this temperature range for about one hour. Product analysis indicated the presence of 5.3% $\text{CF}_3\text{CH}_2\text{Cl}$, 73.0% $\text{CClF}_2\text{CH}_2\text{Cl}$, 14.9% $\text{CCl}_2\text{FCH}_2\text{Cl}$ and 5.3% starting material in addition to minor amounts of other organics.

EXAMPLE 6

Example 5 was repeated except that 15 g of anhydrous HF was used and the internal temperature was maintained at 78-80°C for about two hours with the back pressure regulator set at 500 psig. Product analysis indicated 18.5% $\text{CF}_3\text{CH}_2\text{Cl}$, 75.4% $\text{CClF}_2\text{CH}_2\text{Cl}$ and 5.1% $\text{CCl}_2\text{FCH}_2\text{Cl}$ in addition to small amounts of other organics.

EXAMPLE 7

The General Experimental Procedure was followed using 9.0 g of tetrachloroethylene, 3.0 g of tantalum pentachloride and 7.5 g of anhydrous HF. The reactor was pressurized to 200 psig when cold with nitrogen and the back pressure regulator was set for 500 psig. The contents were heated with stirring at 144-147°C for two hours. Product analysis indicated 66% CF_3CHCl_2 , 32.7% $\text{CClF}_2\text{CHCl}_2$, and small amounts of other organics.

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12. The process of Claim 2 wherein the amount of HF is 5-30 molar equivalents.

13. The process of Claim 2 wherein the alkene is selected from $\text{Cl}_2\text{C}=\text{CCl}_2$, $\text{HClC}=\text{CCl}_2$, $\text{HFC}=\text{CF}_2$,
5 $\text{ClFC}=\text{CF}_2$, $\text{H}_2\text{C}=\text{CCl}_2$, $\text{H}_2\text{C}=\text{CF}_2$, and $\text{H}_2\text{C}=\text{CHCl}$.

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wherein $x = 0$ to 10 , with the proviso that in at least one of R^1 , R^2 , R^3 and R^4 and in at least one of R^5 , R^6 , R^7 and R^8 , Z is F, Br or Cl; and

5 at least one of the pairs R^5 and R^6 , R^7 and R^8 , R^5 and R^7 , and R^6 and R^8 taken together is $-(CH_2)_n-$ wherein " n " is an integer from 2 to 7 with the proviso that when R^5 and R^7 and/or R^6 and R^8 are trans,
10 " n " must be 6 to 7, and when only two of the group R^5 , R^6 , R^7 , R^8 are combined to form a cyclic structure the remaining two groups may be C_xZ_{2x+1} , wherein Z is H, F, Br, or Cl and $x = 0$ to 10 ,

15 with HF in the presence of at least one catalyst selected from tantalum pentachloride and tantalum pentabromide to produce a fluorinated alkane.

3. The process of Claim 2 wherein the amount of HF is 1 to 30 molar equivalents.

20 4. The process of Claim 2 wherein the catalyst is present in an amount of 0.001 to about 5 molar equivalents.

5. The process of Claim 2 wherein the catalyst is tantalum pentachloride.

25 6. The process of Claim 2 wherein the temperature is about 35°C to 175°C .

7. The process of Claim 2 wherein at least two of R^1 , R^2 , R^3 or R^4 are Cl.

30 8. The process of Claim 2 wherein at least three of R^1 , R^2 , R^3 or R^4 are Cl.

9. The process of Claim 2 wherein $x = 1 - 3$.

10. The process of Claim 2 wherein $x = 1$.

35 11. The process of Claim 2 wherein the amount of HF is 3-30 molar equivalents.

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12. The process of Claim 2 wherein the amount of HF is 5-30 molar equivalents.

13. The process of Claim 2 wherein the alkene is selected from $\text{Cl}_2\text{C}=\text{CCl}_2$, $\text{HClC}=\text{CCl}_2$, $\text{HFC}=\text{CF}_2$,
5 $\text{ClFC}=\text{CF}_2$, $\text{H}_2\text{C}=\text{CCl}_2$, $\text{H}_2\text{C}=\text{CF}_2$, and $\text{H}_2\text{C}=\text{CHCl}$.

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